

HIGH TEMPERATURE DEWATERING OF ETHANOL BY VAPOUR PERMEATION AND PERVAPORATION WITH HYBSI® MEMBRANES

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Ethanol is one of the most important commodity chemicals used in a broad range of applications and can be produced by the hydrolysis of ethylene, though by far the largest fraction of ethanol is produced via fermentation mainly using 1st generation feedstock. Regardless of the source of the ethanol, from fermentation or from direct hydration of ethylene, the product is normally a dilute aqueous solution. The product is fed to a distillation system to concentrate ethanol. The separation of ethanol and water is complicated because ethanol and water form an azeotrope at 95.6 weight% ethanol. It is not possible to produce pure ethanol from an azeotropic mixture by normal distillation.

Pervaporation is a method for dehydration of organics such as ethanol, which substantially avoids drawbacks of azeotropic distillation and adsorption. As the pervaporation process is not governed by thermodynamic equilibria and the selectivity is determined by the difference in permeation rates of components through the membrane, mixtures of components with close boiling points and azeotropic mixtures can be effectively separated. Pervaporation exhibits its highest efficiency in a concentration range of the ethanol-water mixture where distillation is least effective, namely, at high ethanol concentrations of 90-95 wt.%, especially in the vicinity of the azeotropic concentration.

Previous studies have shown that hybrid distillation processes combined with either pervaporation or vapour permeation can be very attractive for the separation of liquid mixtures. Such a hybrid process leads to large energy savings when the membrane is used for breaking the azeotrope. At the preferred process conditions currently available commercial polymer and zeolite membranes cannot be used. In this study, the focus is on membrane stability at higher operating temperatures in a water ethanol mixture for sol-gel derived Hybsi® membranes and the membrane performance in pervaporation and vapour permeation. The stability of the membranes is one of the crucial factors of their application in industrial separation processes. A comparison between pervaporation and vapour permeation has been made in which water removal from ethanol has been used as an example. By applying higher temperatures and thus higher driving forces in the membrane unit the required membrane area and the total costs of the process are strongly reduced. The comparison was based on endurance tests, in the dehydration of ethanol at 150°C. The high hydrothermal and chemical stability of the membrane was proven in continuous measurements (24/7) that lasted for periods of over 500 days. The membrane performance was followed during this period of time by measuring the flux and membrane selectivity. Both in pervaporation and vapour permeation a good and stable membrane performance was obtained after a stabilisation period and from a flux and selectivity point of view at 150°C both membrane operation options show similar results. Detailed test results will be presented. For ethanol dehydration vapour permeation would be preferred above pervaporation as advantage can be taken of the vapour already present at the top of the distillation column which will still be used to remove major part of the water present.

The presented results show that HybSi® membranes are applicable in the dehydration of ethanol by pervaporation and vapour permeation at higher temperatures. The high temperature use leads to a broadened application window and will open up markets that have so far been inaccessible for commercially available pervaporation and vapour permeation membranes.